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Fundamental research on actinide materials for sustainable fuel cycles in JAEA

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Abstract

The fundamental research on actinide materials has been carried out in order to contribute to the development of future nuclear fuel cycle and actinide science database. Among actinide materials, the R&D has been focused on Pu and minor actinide (MA; Np, Am, Cm) bearing compounds. The chemical forms of actinide compounds concerned include oxides, nitrides, chlorides and alloys, which are prepared, characterized and subjected to property measurements. In this paper those results on Pu and MA bearing oxides obtained in recent several years are summarized. In addition, the possible challenges of actinide materials research to the subjects of post severe accident of Fukushima-daiich nuclear power station are briefly discussed.

Keywords: Plutonium; minor actinides; neptunium; americium; curium; oxygen potential; thermal conductivity; oxide fuel

1. Introduction

In Japan Atomic Energy Agency (JAEA), the fundamental research on actinide materials has been carried out in order to contribute to the development of future nuclear fuel cycle and actinide science database. Among actinide materials, the R&D has been focused on Pu and minor actinides (MA; Np, Am, Cm) bearing compounds, since they have several different characteristics from U bearing compounds. The chemical forms of actinide compounds concerned include oxides, nitrides, chlorides and alloys, which are prepared, characterized and

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subjected to property measurements. In this paper, those results on Pu and MA bearing oxides obtained in recent several years are summarized.

Pu and MA oxides are characterized by CaF_2-type dioxides having a single-phase region in hypostoichiometry, MO_{2-x} (M; Pu or MA), and sesquioxides, M_2O_3, accompanied with phase transformations. In regard to CaF_2-type actinide dioxides, the higher the atomic number of actinides, the less thermodynamically stable the dioxides are in general. The R&D will contribute to the development of not only MA-MOX fuel based on homogeneous recycling but also MA oxide fuel based on heterogeneous recycling in future nuclear fuel cycle. Especially, the addition of Am and Cm to U or U-Pu oxide fuel has a large impact on several properties, since they are likely to be reduced from tetravalent to trivalent states, resulting in hypostoichiometric composition under the same oxygen potential. Therefore, the dependences of oxygen potential on O/M ratio, temperature and crystal structure were investigated for Pu and MA bearing oxides. The dependences of thermal conductivity on composition and temperature were obtained from the measured thermal diffusivity and heat capacity. The degradation of thermal conductivity by self-irradiation damage was also evaluated. Further, the thermal conductivity of CERMET and CERCER fuels was calculated by use of finite element method (FEM).

Lastly, the possible challenges of actinide materials research to the subjects of post severe accident of Fukushima-daiichi nuclear power station (1F) are briefly discussed.

2. R&D on Pu and MA oxides

2.1 Oxygen potential

The oxygen potential is an essential property for evaluating thermodynamic behaviour of oxide fuel both in fabrication and irradiation stages. The relations between the oxygen potential and composition, temperature, crystal structure and so on were investigated; AmO_{2-x} [1], $(Am,Np)O_{2-x}$ [2], $(Am,Pu)O_{2-x}$ [3] and $(Cm,Pu)O_{2-x}$ [4] with CaF_2-type structure and $Am_2Zr_2O_{7+y}$ [5] with pyrochlore structure were subjected to the oxygen potential measurements by electromotive force (EMF) method utilizing a zirconia solid electrolyte. The galvanic cell type is expressed by

(Pt electrode) Sample / $Zr(Ca)O_{2-x}$ / air (Pt electrode).

Then the oxygen potential of the sample is given by the following Nernst equation,

$$g(O_2) = 4FE + RT \ln P_{air(O2)} \quad (1)$$

where $g(O_2)$ is the oxygen potential of the sample, F the Faraday constant, E the potential difference between two Pt electrodes, R the gas constant, T the temperature in Kelvin and $P_{air(O2)}$ the partial pressure of oxygen in air. Prior to the measurements of Pu and MA oxides, the experimental system was checked by use of CeO_{2-x} as a reference material.

It was found that the oxygen potential of AmO_{2-x} was higher than that of CeO_{2-x} by about 200kJ/mol at $1.5<O/M<2.0$, although they showed the similar O/M dependence between 1000 and 1333K [1]. Further, the presence of the intermediate phases of Am_9O_{16} and Am_7O_{12} was suggested. It was found that the oxygen potential of $(Am_{0.5}Np_{0.5})O_{2-x}$ smoothly decreased with O/M from 1.98 to 1.75 at 1333K, which suggested that the sample kept a single phase of CaF_2-type structure [2]. At O/M=1.75 where the chemical composition could be expressed as $(Am^{3+}_{0.5}Np^{4+}_{0.5})O_{1.75}$, however, it suddenly decreased from about -440kJ/mol. This phenomenon could be attributed to the further reduction of Am^{3+} to Am^{2+} or Np^{4+} to Np^{3+} at O/M below 1.75. On the other hand, the oxygen potential of $(Am_{0.5}Pu_{0.5})O_{2-x}$ showed the similar O/M dependence with AmO_{2-x} [3]. It smoothly decreased from -80 to -360kJ/mole with O/M from 1.98 to 1.78, but remained almost constant at around

O/M=1.77. Therefore, it was suggested that the sample was composed of the single phase of CaF_2-type structure at 1.78<O/M<1.98 but the mixed phases of CaF_2-type structure and $(Am,Pu)_9O_{16}$ at around O/M=1.77.

The results for AmO_{2-x}, $(Am_yNp_{1-y})O_{2-x}$ and $(Am_yPu_{1-y})O_{2-x}$ at 1333K are summarized in Fig. 1, in which the oxygen potential is plotted against Z(=x/y) denoting a molar ratio of Am^{3+} to all Am ions. As far as the samples have the single phase of CaF_2-type structure, the oxygen potentials show the similar Z dependence. Therefore, it is suggested that the oxygen potentials only depend on the ratio of Am^{3+}/Am when Np or Pu has the valence state of 4+ in $(Am,Np)O_{2-x}$ or $(Am,Pu)O_{2-x}$ with CaF_2-type structure, as is the case of $(Pu,U)O_{2-x}$, in which the oxygen potential only depends on the ratio of Pu^{3+}/Pu.

On the other hand, Fig. 2 shows the O/M dependence of the oxygen potential of $(Cm_{0.09}Pu_{0.91})O_{2-x}$ at 1173, 1213, 1253, 1293 and 1333K. At all temperatures, the O/M dependence changes at O/M=1.955 although the sample keeps the single phase of CaF_2-type structure. In this case it is suggested that the oxygen potential decreases with O/M from 1.98 to 1.955 following the reduction of Cm^{4+} to Cm^{3+} in $(Cm^{3+},Cm^{4+},Pu^{4+})O_{2-x}$, and it decreases with O/M below 1.955 following the reduction of Pu^{4+} to Pu^{3+} in $(Cm^{3+},Pu^{3+},Pu^{4+})O_{2-x}$.

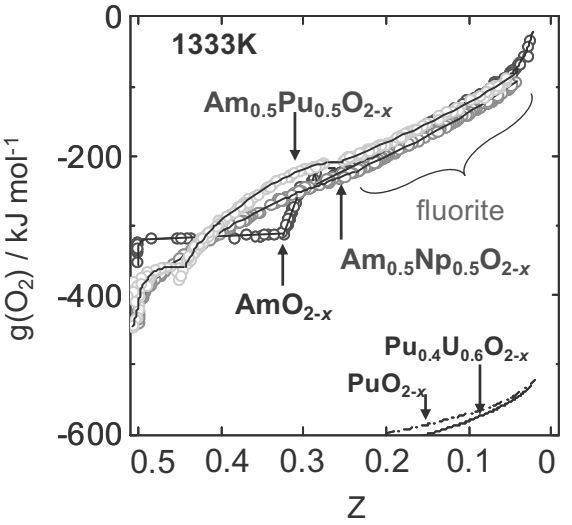

Fig. 1 Z(=x/y) dependences of oxygen potential of AmO_{2-x}, $(Am_yNp_{1-y})O_{2-x}$ and $(Am_yPu_{1-y})O_{2-x}$ at 1333K

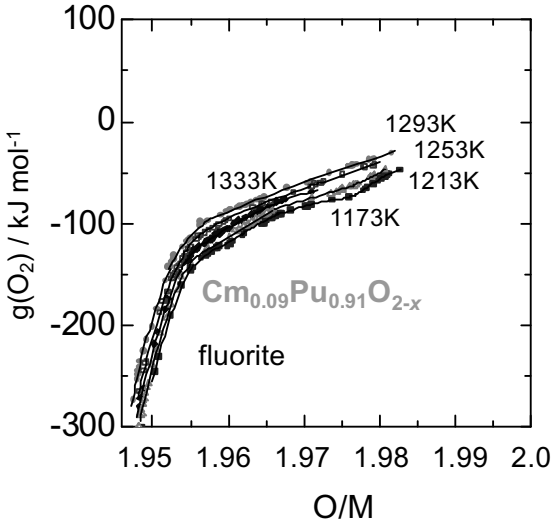

Fig. 2 O/M dependences of oxygen potential of $(Cm_{0.09}Pu_{0.91})O_{2-x}$ at 1173, 1213, 1253, 1293 and 1333K

2.2 Thermal conductivity

The thermal conductivity of Pu and MA oxides is derived from the thermal diffusivity and heat capacity measured by laser flash method and drop calorimetry, respectively; NpO_2 [6], AmO_2 [7], AmO_{2-x} [8], $(Pu,Am)O_2$ [9], $(Pu,Am)O_{2-x}$ [9], $(Pu,Cm)O_2$ [10] and Am_2O_3 [7] were subjected to the measurements. The thermal diffusivity measurement of the stoichiometric dioxide often faces the difficulty at high temperatures, since Pu, Am and Cm ions are likely to be reduced from tetravalent to trivalent states in vacuum resulting in the decrease of O/M ratio. Therefore, the measurements of stoichiometric AmO_2, $(Pu,Am)O_2$ and $(Pu,Cm)O_2$ were limited to the temperature range below 773K.

Fig. 3 shows the temperature dependence of the thermal conductivity of NpO_2 [6], AmO_2 [7], AmO_{2-x} [8] and Am_2O_3 [7] together with that of UO_2 [11] and PuO_2 [12] in literatures. It is seen that NpO_2 and AmO_2 have the similar thermal conductivity in the temperature below 773K. The thermal conductivity of AmO_{2-x}, in which the O/M ratio was evaluated to be approximately 1.73, is much lower than that of stoichiometric AmO_2. Further, the thermal conductivity of Am_2O_3 with La_2O_3-type structure is about one-half of that of AmO_2 although it has the similar temperature dependence with that of actinide dioxides with CaF_2-type structure.

On the other hand, Fig. 4 shows the storage duration dependence of the thermal conductivity of $(Pu_{0.91}Cm_{0.09})O_2$ at 473, 523 and 573K, in which the self-irradiation damage does not recover [10]. It is found that the thermal conductivity remarkably decreases with the storage duration due to the accumulation of the self-irradiation damage mainly caused by ^{244}Cm with a half life of 18.1y. In this case the decrease of thermal conductivity ΔK by storage could be approximated by the following self-irradiation lattice expansion model,

$$\Delta K = A[1-\exp(-B\lambda t)] \quad (2)$$

where λ is the effective decay constant of actinides, t the storage duration after sintering, and A and B the constants determined from the linear expansion of the lattice parameter of $(Pu_{0.91}Cm_{0.09})O_2$.

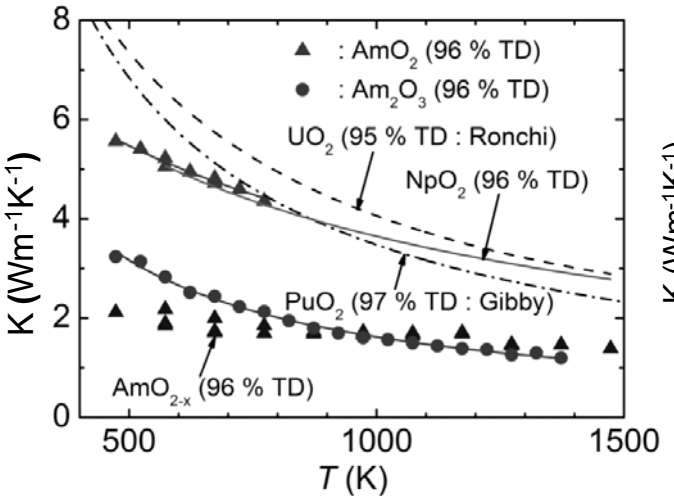

Fig. 3 Temperature dependences of thermal conductivity of NpO_2, AmO_2, AmO_{2-x} and Am_2O_3 together with UO_2 and PuO_2 in literatures

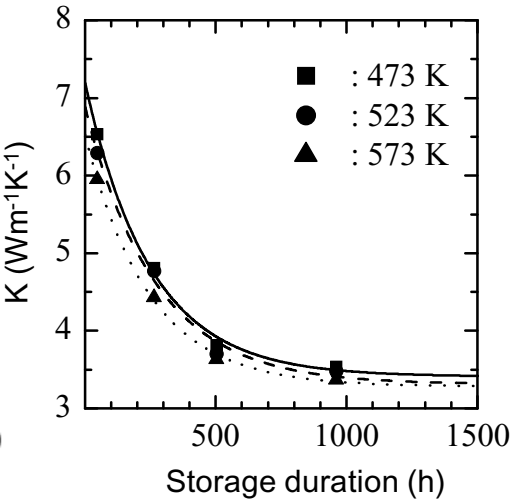

Fig. 4 Storage duration dependences of thermal conductivity of $(Pu_{0.91}Cm_{0.09})O_2$ at 473, 523 and 573K

The thermal conductivity of $(Am_{0.5}Pu_{0.5})O_2$ and $(Am_{0.5}Pu_{0.5})O_{2-x}$ was measured by the same method mentioned above [9]. Using the measured thermal conductivity and literature values for Mo and MgO, the thermal conductivity of Mo-based CERMET and MgO-based CERCER fuels was calculated by FEM under the joint research with Osaka University [13]. Figs. 5 and 6 show the temperature dependences of the thermal conductivity of Mo-based CERMET fuels containing 20 and 40vol% of $(Am_{0.5}Pu_{0.5})O_{1.75}$ and those of MgO-based CERCER fuels calculated by FEM, respectively, together with the measured thermal conductivity of $(Am_{0.5}Pu_{0.5})O_{1.75}$. It is seen that the low thermal conductivity of $(Am_{0.5}Pu_{0.5})O_{1.75}$ is remarkably improved by adopting CERMET or CERCER fuel.

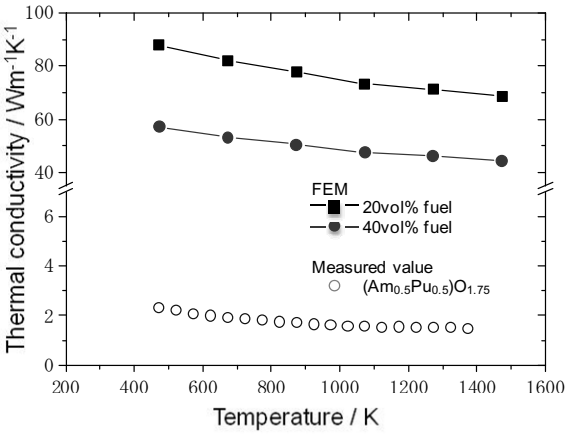

Fig. 5 Temperature dependences of thermal conductivity of Mo-based CERMET fuels calculated by FEM together with measured thermal conductivity of $(Am_{0.5}Pu_{0.5})O_{1.75}$

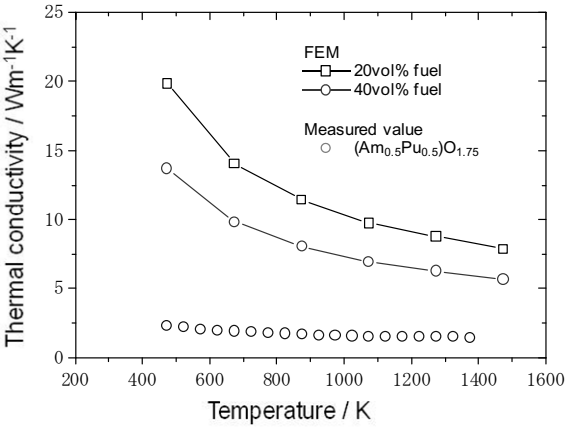

Fig. 6 Temperature dependences of thermal conductivity of MgO-based CERCER fuels calculated by FEM together with measured thermal conductivity of $(Am_{0.5}Pu_{0.5})O_{1.75}$

3. Challenges to the subjects of post severe accident of Fukushima

In a severe accident of 1F happened in March 2011, the fuels in three reactors (Unit 1, 2 and 3) were severely damaged by the loss of all AC power supply (SBO) after the attack of heavy tsunami. It is considered that a large-scale fuel melting occurred and some part of the melt reached the bottom of the primary containment vessel (PCV) through the reactor pressure vessel (RPV).

According to the preliminary roadmap of Japanese government and Tokyo Electric Power Company (TEPCO), the removal of fuel debris from RPV and PCV will start about 10 years later. In that case, however, the decontamination of reactor building, repair of RPV and PCV, holding water into RPV and PCV, and sampling and inspection of fuel debris have to be finished by that time. Several R&D has been launched for the restoration, decontamination and decommissioning.

From the viewpoints of material science, in contrast to the severe accident of TMI-2 in 1979, that of 1F is characterized by the follows; core structure and material composition particular to BWR, higher burnup and MOX fuel (only Unit 3), longer period without enough cooling leading to a large-scale fuel melting, pumping sea water into the core, possibly Molten Corium and Concrete Interaction (MCCI) and so on. Challenges of actinide materials research to the subjects of post severe accident of 1F have been discussed and planned in JAEA, although most of them are rather primitive. They include thermodynamic re-evaluation of U-Zr-O system, fabrication and characterization of simulated fuel debris including the effect of sea water, colloid chemistry of U and Pu oxides, and release behaviour of less volatile fission products (FP) than I and Cs under the fuel melting condition and so on.

4. Conclusion

Recent results on actinide materials research in JAEA were summarized. The oxygen potentials of Pu and MA bearing oxides including their solid solutions were measured by EMF technique. The effects of composition, temperature and crystal structure on the oxygen potential were discussed. The thermal conductivities of Pu and MA bearing oxides were derived from the thermal diffusivity and heat capacity measured by laser flash method and drop calorimetry, respectively. It was found that the effect of O/M ratio is much larger than that of the sort

of actinide elements, and the self-irradiation damage caused by Cm remarkably deteriorates the thermal conductivity. Further, the thermal conductivities of CERMET and CERCER fuels containing $(Am,Pu)O_{2-x}$ were evaluated by FEM. Hereafter, the actinide materials research should contribute to the subjects of post severe accident of 1F besides the development of future nuclear fuel cycle.

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